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(19)(CA) # CANADIAN PATENT

(54) ALKALINE EXTRACTION OF LIGNINS IN NITRIC ACID PULPING

(72) Kalisch, John H., Hawkesbury, Ontario, Canada

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ALKALINE EXTRACTION OF LIGNINS IN NITRIC ACID PULPING

Abstract of the Disclosure

By extracting nitric acid pulped cellulosic materials with a mixture containing a major amount of ammonium hydroxide and a minor amount of sodium hydroxide an increase in pulp yield is obtained beyond that which is obtained when either sodium hydroxide or ammonium hydroxide is used alone.

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By extracting nitric acid pulped cellulosic materials with a mixture containing a major amount of ammonium hydroxide and a minor amount of sodium hydroxide an increase in pulp yield is obtained beyond that which is obtained when either sodium hydroxide or ammonium hydroxide is used alone.

This invention relates to nitric acid pulping of cellulosic containing materials and, more particularly, to an improvement in the alkaline extraction stage which results in increased pulp yields.

A great variety of nitric acid pulping processes are known. A description of such processes can be found in the Journal of the Technical Association of the Pulp and Paper Industry (TAPPI), Vol. 50, No. 12, pgs. 44A-51A, December 1967. All such processes are based on a minimum of two pulping stages. In the first stage the pulp is reacted with nitric acid in a concentration range of from about 5% to about 40% and at a temperature of from about 45°C. to about 95°C. Since the nitric acid stage does not solubilize enough lignin to complete pulping, another stage is required. During this stage the remaining insolubilized lignins are solubilized by extraction with an alkaline compound to complete the pulping

operation.

Usually sodium hydroxide is used to extract the lignins. It has also been proposed that aqueous ammonium hydroxide be used in extracting the nitric acid treated wood chips. (See TAPPI, Vol. 44, No. 4, pgs. 263-271, April, 1961.) A disadvantage connected with the use of an ammonium hydroxide extraction stage is that the pulping is incomplete unless a much more severe nitric acid treatment precedes the extraction stage. A more severe nitric acid treatment results in increased cellulose degradation and higher nitric acid consumption. Furthermore, more degraded pulps do not lend themselves to normal bleaching practice and also exhibit inferior paper properties.

It has now quite unexpectedly been found that by using a mixture consisting of a major amount of ammonium hydroxide and a minor amount of sodium hydroxide during the alkaline extraction stage, a satisfactory pulp results without having to resort to a severe nitric acid treatment in the first stage. It has been found that this improvement unexpectedly results in significant increases in pulp yield ranging from about 5% to about 10%.

The above-noted advantages are obtained where the concentration of the sodium hydroxide in the mixture is from about 5% to about 20% of the concentration of the ammonium hydroxide. This small amount of sodium hydroxide is sufficient to increase the initial pH of the extraction liquor from 12 to 13 and produce the beneficial results referred to previously. This is completely unexpected in view of the results obtained when either sodium hydroxide alone or ammonium hydroxide alone are used in the extraction stage.

The source of cellulosic material can be standard wood chips or wafers, or sawdust or shavings, obtained from either hardwoods or softwoods, such as are ordinarily used in a pulp or

paper mill.

The nitric acid first stage of the present invention involves rapid impregnation of the wood. This is achieved by either submersed compression and immediate expansion of mill chips in nitric acid or by impregnation of thin wafer chips in nitric acid under atmospheric conditions.

Using nitric acid having a concentration of about 14% and a liquor-to-wood ratio (L:W) of about 4:1, the nitration is completed in about one hour when conducted at 55°C.

The nitric acid is then drained for reuse and in a second stage the impregnated chips are then either heated with water for 90 minutes at 95°C. at a L:W ratio of 4:1 or heated atmospherically with steam in a vapor phase for about 55 minutes at about 98°C.

After briefly washing the chips with fresh water, the chips are subjected to the novel alkaline extraction stage of the present invention.

The concentration of the ammonium hydroxide in the ammonium hydroxide-sodium hydroxide mixture used to treat the chips can be from about 2% to about 10%, with a concentration of 5% being preferred. The concentration of the sodium hydroxide in said ammonium hydroxide-sodium hydroxide mixture can be from about 5% to about 20% of the concentration of the ammonium hydroxide, with a concentration of from about 10% to about 15% being preferred, and 12% especially preferred.

The following examples will aid in illustrating the process of the present invention.

EXAMPLE 1

White birch wafer chips having a moisture content of 34% were treated with nitric acid in accordance with the following process conditions.

Nitric Acid Stage

Nitric Acid, Conc. %	14
Liquor to wood ratio	5:1
Temperature, °C	55
Time at 55°C, minutes	60

Nitric acid consumption during this stage was 20.4% on wood. The concentration of the acid after this stage was 10.8%.

The acid was drained and is reused after bringing it up to strength.

Hot Aqueous Stage

After draining the acid, the chips were treated with hot water in accordance with the following process conditions.

Water:wood ratio	4:1
Temperature, °C	95
Time at 95°C, minutes	90
Residual HNO_3 in spent aqueous solution, %	0.4

After completion of the hot aqueous stage, the chips were briefly washed with fresh water.

The chips were then divided into three equal lots (a), (b) and (c) and subjected to three different alkali extraction procedures as set forth below. The pulp properties are listed below in Tables I and II.

Alkaline Extraction Stage

	(a) NaOH Type	(b) NH_4OH Type	(c) NH_4OH + NaOH Type
NaOH, conc., %	3		0.6
NH_4OH conc., %		5.1	5.0
Liquor:wood ratio	4:1	8:1	4:1
Temperature, °C.	95	85	95
Time at temp., min.	60	60	60
pH at start	13.1	12.0	13.1
Terminal pH	12.7	10.4	10.0

TABLE I

Screened pulp yield, %	47.3	38.5-very shivy pulp	54.1
Screenings, % on wood	0.6	10.0	1.0
Lignin, %	0.6	2.4	0.7
Alpha Cellulose, %	88.2	84.8	84.0
Pentosans, %	12.5	22.5	20.7
Resin, %	0.17	0.25	0.3
Brightness, % MgR	53.4	29.1	37.1
Viscosity, CED, CPS.	46	41	36.0

TABLE II

Strength at 500 ml CSF

Breaking length, M	9200	9400
Tear Factor	75	63
Time to 500 CSF, min. (PFI-mill)	1.62	0.96

All above pulps prepared according to alkaline treatments (a), (b) and (c) were opened up in their own liquor by means of a "Lightnin"* mixer, then washed free of spent liquor and screened on a 12 cut Valley Iron Flat screen.

EXAMPLE 2

A blend of softwood sawdust-shavings of sawmill origin was subjected to a pretreatment by steaming at 100°C. for ten minutes, and was then treated with nitric acid in accordance with

* Trademark

the following process conditions.

Nitric Acid, conc., %	14.2
Liquor:wood ratio	4.2:1
Temperature, °C.	75
Time at 75°C, minutes	60

The nitric acid consumption during this stage was 39.1% on wood. The concentration of the acid after this stage was 7.5%.

The acid was drained and is reused after bringing it up to strength.

Vapor Phase Stage

After draining the acid, the chips were steamed under atmospheric pressure in accordance with the following process conditions.

Steaming time, minutes	180
Temperature, °C	100

After completion of the vapor phase stage, the chips were briefly washed with fresh water.

The chips were then divided into equal lots (a) and (b) and subjected to two different alkali extraction procedures as set forth below. The pulp properties are listed below in Tables III and IV.

Alkaline Extraction Stage

	(a) NaOH Type	(b) NH_4OH + NaOH Type
NH_4OH, conc., %		5.0
NaOH, conc., %	3	0.6
Liquor:Wood ratio	4	4
Temperature, °C	95	80
Time at temperature, min	60	60
pH at start	13.1	13.1
Terminal pH	12.4	10.4

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TABLE III

	(a) NaOH Type	(b) NH_4OH + NaOH Type
Screened pulp yield, %	39.3	48.9
Screenings, % on wood	0.7	1.0
Lignin, %	1.0	2.2
Alpha-Cellulose, %	87.9	83.4
Resin, %	0.06	0.26
Brightness, % ELR	34.4	25.1
Viscosity, CED, cps	16.7	13.9
Pentosan, %	5.3	5.2
Mannan, %	5.8	8.6

Table IV

Strength at 300 ml CSF		
Breaking Length, M	7600	8000
Tear Factor	45	40
Time to 300 CSF, min (PFI-mill)	0.74	0.51

All above pulps prepared according to alkaline treatments (a) and (b) were opened up in their own liquor by means of a "Lightnin" mixer, then washed free of spent liquor and screened on a 12 cut Valley iron flat screen.

Examples 1 and 2 illustrate that an increase in the initial pH resulting from a small addition of NaOH to NH_4OH cannot be the only reason for the effectiveness of the mixture in increasing pulp yield. A comparison of alkaline extractions according to (a) and (c) in Example 3 and (a) and (b) in Example 2 show identical initial extraction pH's. It is shown in the examples in Tables I and III that the NH_4OH - NaOH mixture resulted in a considerably higher retention of hemicelluloses than by sodium hydroxide alone at comparable pH. On the other hand, Table I shows that, although ammonium hydroxide

extraction alone is able to contribute to increased pentosan retention, the pulping effect remains incomplete as demonstrated by low screened yield, high screenings and higher lignin. Consequently, it appears that a synergistic effect produced by a combination of the two alkaline compounds is responsible for the benefits obtained.

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The embodiments of the present invention in which an exclusive property or privelege is claimed are described as follows:

1. In the process of pulping cellulosic materials involving a rapid impregnation of the cellulosic material with nitric acid in the first stage, followed by a water or water vapor second stage, and an alkaline extraction in the third stage, the improvement in the alkaline extraction stage resulting in increased yield which comprises treating the cellulosic material in an aqueous alkaline solution with a mixture of ammonium hydroxide and sodium hydroxide, the concentration of said ammonium hydroxide being from about 2% to about 10%, based upon the concentration of the extractant solution, and the concentration of said sodium hydroxide being from about 5% to about 20% of the concentration of the ammonium hydroxide.

2. The process as recited in claim 1 wherein the concentration of the ammonium hydroxide is about 5%, and the concentration of the sodium hydroxide is from about 10% to about 15%, based on the concentration of the ammonium hydroxide.

SUBSTITUTE

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